Chapter 15
Interfacial Phenomena

In this chapter, we will discuss how the chemical and physical properties of substances at interfaces differ from those in the bulk. For quantitative description, quantities like surface tension and surface energy have to be introduced. With the help of these quantities, phenomena known from everyday life like the lotus effect can be explained. However, perhaps you are more interested to learn how detergents clean? Then have a look at Sect. 16.3 which deals with the adsorption on liquid surfaces. The next section covers the adsorption on solid surfaces and the variation of the extent of coverage with pressure or concentration of the substance to be adsorbed. Langmuir's isotherm, the simplest description of such an adsorption process, is deduced by kinetic interpretation of the adsorption equilibrium. Alternatively, it can be derived by introducing the chemical potential of free and occupied sites and considering the equilibrium condition. In the last part of the chapter, some important applications such as surface measurement and adsorption chromatography are discussed.

15.1 Surface Tension, Surface Energy

The *interface* is defined as the layer separating two phases. The interface adjacent to a gas phase is also simply called a *surface*.

The particles at an interface between two phases, for example, those on the surface of a solid or liquid, are subject to different intermolecular forces than those inside a phase (Fig. 15.1). A particle inside a phase is attracted equally on all sides by identical neighboring particles. This means that intermolecular forces are in equilibrium and the net attractive pull on the particle in question equals zero. Particles at an interface such as between a solid and air or between a liquid and air are missing part of their neighbors. This leads to an imbalance of forces where (especially in the case of surfaces) a one-sided pull occurs toward the interior of the denser phase. Consequently, the neighboring particles in the interface will move

G. Job, R. Rüffler, *Physical Chemistry from a Different Angle*,
DOI 10.1007/978-3-319-15666-8_15

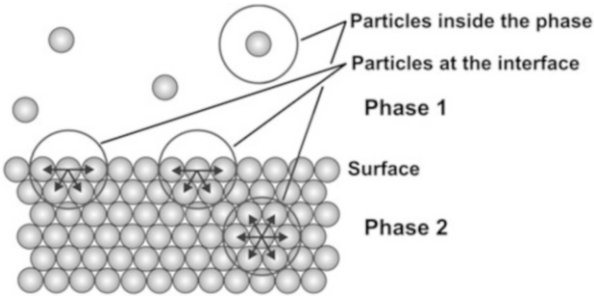
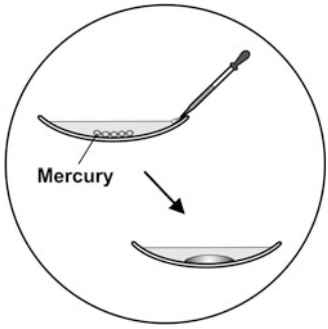


Fig. 15.1 Model of the surface of a condensed phase (solid or liquid).



Experiment 15.1 *Merging of droplets of mercury*: Small droplets form when dripping mercury in a watch-glass filled with ethanol. They will gradually merge to form one large drop.

somewhat closer together and a tensile stress in the surface layer will appear (comparable to that in a stretched rubber membrane). This phenomenon is called *interfacial tension* or *surface tension* and is abbreviated by σ.

Surface tension results in a tendency for drops of liquid or gas bubbles to minimize their surface areas. If there are no other forces such as gravity at work, they will assume a spherical shape because a sphere has the smallest surface area for a given volume. Large drops grow at the cost of smaller ones because this also leads to a minimizing of the total surface area (Experiment 15.1).

The tensile forces F_σ that appear most noticeably at the boundary lines of the surface are proportional to the length l of such a contact line:

$$F_\sigma \sim l.$$

Therefore we define

$$\text{Surface tension} := \frac{\text{Tensile force}}{\text{Contact line}} \quad \text{or} \quad \sigma := \frac{F_\sigma}{l}. \tag{15.1}$$

The SI unit for surface tension σ is N m^{-1}.

To increase the surface area by ΔA, an amount of energy $W_{\rightarrow A}$ is needed because of the surface tension σ. Interpreted atomistically, molecules are transported against the tensile forces from inside the phase to its surface and this costs energy. The molecules at the surface of the phase therefore have an amount of energy that is

higher by the *surface energy* $W_{\rightarrow A}$ than the energy of the molecules inside the phase. Surface tension can also be understood as surface energy density.

The concept of surface tension can be illustrated by a liquid film (such as a soap film) between a U-shaped wire frame and a slider (moveable piece of wire), comparable to a two-dimensional cylinder and piston (Fig. 15.2).

l is the total width of the surface on the front and the back of the liquid film. The slider with the weight hanging from it keeps the system in equilibrium. The weight F_G just compensates for the force F_σ that tries to contract the film.

In order to increase the liquid surface of the film by the small amount $dA = l \cdot ds$, the slider is shifted downward using only slightly more force than F_σ. The force needed is independent of the starting position of the slider and therefore of the size of the surface. This would be different when expanding a rubber membrane where the applied force increases with the elongation. The energy necessary results in

$$dW_{\rightarrow A} = F_\sigma ds = \sigma \cdot l \cdot ds \quad \text{or finally} \quad dW_{\rightarrow A} = \sigma dA. \tag{15.2}$$

After transforming the expression we arrive at what we wanted to show,

$$\sigma = \frac{dW_{\rightarrow A}}{dA}.$$

An interface can be understood to be a separate phase with an area A but not a volume ($V = 0$). We will not go into this right now. The main equation (Sect. 9.1) for such an "interface phase" where substances can be enriched from the neighboring phases, or can migrate into those phases, is:

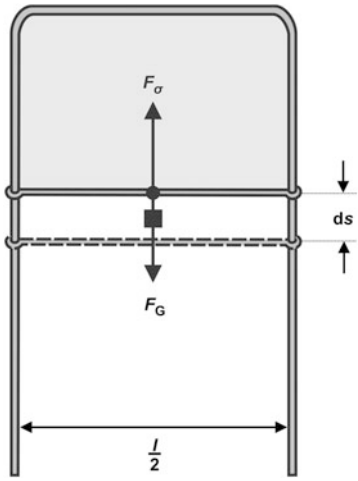


Fig. 15.2 Illustration of surface tension using a soap film in a wire frame with a slider.

Experiment 15.2 *Soap film*: When the slider is slowly pulled away from the end of the frame (see the *hand symbol*), the soap film expands. If we let go, the film contracts to its former size and the slider moves back to its original position (note the *arrow*).

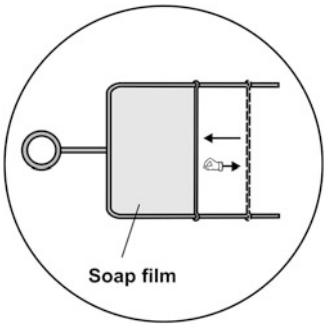


Table 15.1 Surface tensions of various liquids at 298 K (from: Lide D R (ed) (2008) CRC Handbook of Chemistry and Physics, 89th edn. CRC Press, Boca Raton).

Liquid	σ (mN m^{-1})
Diethyl ether	16.7
n-Hexane	17.9
Ethanol	22.0
Carbon tetrachloride	23.4
Acetic acid	27.1
Benzene	28.2
Water	72.0
Mercury	485.5

Table 15.2 Surface tension of water at various temperatures (from: Lide D R (ed) (2008) CRC Handbook of Chemistry and Physics, 89th edn. CRC Press, Boca Raton).

Temperature (K)	σ (mN m^{-1})
283	74.2
298	72.0
323	67.9
348	63.6
373	58.9

$$dW = \sigma dA + TdS + \sum_i \mu_i dn_i. \tag{15.3}$$

The sum $\sum \mu_i n_i$ can be left out if we are only dealing with a pure substance. The main equation then becomes especially simple.

The effects of surface tension can be observed concretely in an experiment (Experiment 15.2).

Surface tension is a substance-specific quantity. For many organic liquids, at around 298 K, it is between 15 and 30 mN m^{-1} (Table 15.1). The much higher value of $\sigma = 72$ mN m^{-1} for water is due to the high polarity of water molecules and the resulting relatively strong hydrogen bridge bonds between them. Surface tension of mercury is even six times higher than that of water. This is because of the metallic bonds between the atoms.

Surface tension decreases when temperature increases because the more intense motion of the molecules leads to a lessening of the intermolecular forces. It disappears when the critical point is reached. Table 15.2 shows the surface tension of water at various temperatures.

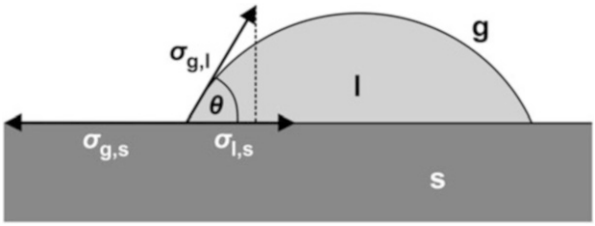


Fig. 15.3 Overlapping of different interface tensions and the corresponding contact angle (or wetting angle) θ of a liquid drop on a plane solid surface.

15.2 Surface Effects

Wetting Wetting is defined as the complete covering of a solid surface by a liquid film caused by the attractive forces between different substances at a common interface.

If a drop of liquid is put upon a solid surface, three phases adjoin each other: gaseous (g), liquid (l), and solid (s) (Fig. 15.3).

Relating to a short section of length l of the three-phase contact line (which in this case is perpendicular to the plane of the drawing), we have to consider three interface tensions: $\sigma_{g,l}$, $\sigma_{g,s}$, and $\sigma_{l,s}$. As a result, three forces $\sigma_{g,l} \cdot l$, $\sigma_{g,s} \cdot l$, and $\sigma_{l,s} \cdot l$ act parallel to the arrows in Fig. 15.3. The contact line shifts right or left, and in doing so, the *contact angle* θ changes accordingly until equilibrium of forces is attained. A shift upward is impossible due to the rigid base, so we only need to consider the force components that are parallel to the solid surface:

$$\sigma_{g,s} \cdot l = \sigma_{l,s} \cdot l + \left(\sigma_{g,l} \cdot \cos\theta\right) \cdot l \text{ or } \sigma_{g,s} = \sigma_{l,s} + \sigma_{g,l} \cdot \cos\theta. \tag{15.4}$$

If $\theta < 90°$, the liquid will spread across the solid surface; it *wets* the surface. Complete wetting exists when $\theta = 0°$ (or $\sigma_{g,s} > \sigma_{l,s} + \sigma_{g,l}$; in this case, an equilibrium of force is impossible). Water on greaseless glass shows a contact angle of $\approx 0°$.

If, however, $\theta > 90°$ (in the ideal case, 180°), no wetting will take place (Fig. 15.4) [Examples: mercury on glass, water on lotus leaves (lotus effect), water on polytetrafluoroethene fabric (Gore-Tex®)].

Capillary Pressure Capillary pressure corresponds to excess pressure p_σ in a gas bubble or a drop as a result of interface tension. Experiment 15.3 will serve to clarify this.

Apparently, capillary pressure decreases as the radius increases. How can this be explained? There is an excess pressure p_σ inside a bubble, which balances the interface tension. If the radius r grows by dr due to further inflating of the bubble, thereby increasing volume V by $dV = 4\pi r^2 dr$, the energy to be expended is

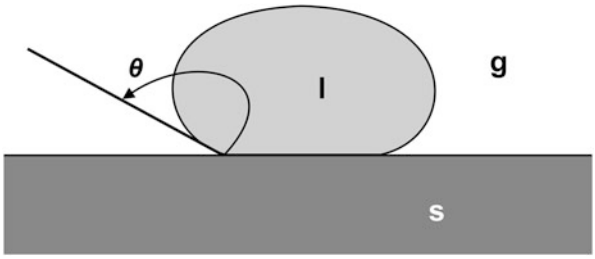
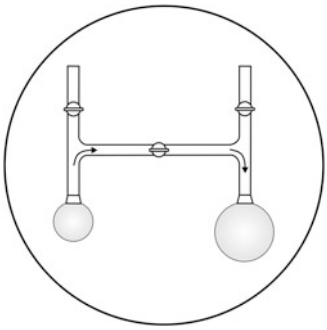


Fig. 15.4 Lack of wetting of the surface at a contact angle of $\theta > 90°$.



Experiment 15.3 *Connected soap bubbles*: Two soap bubbles of differing sizes are connected via a closed stopcock. When the stopcock is opened, the smaller bubble will "inflate" the larger one and disappear in the process.

$$\mathrm{d}W = p_\sigma \mathrm{d}V = p_\sigma \cdot 4\pi r^2 \mathrm{d}r.$$

At the same time, the surface of the bubble grows by $\mathrm{d}A = 8\pi r \mathrm{d}r$ and the surface energy grows along with it. However, in the case of a soap bubble, there are both an inner and an outer surface to be dealt with. This means that, in total, the change of surface energy is:

$$\mathrm{d}W_{\to A} = \sigma \mathrm{d}A = \sigma \cdot 16\pi r \mathrm{d}r.$$

The volume of a sphere is $4/3\pi r^3$ and its surface is $4\pi r^2$. By taking the derivative, we obtain

$$\frac{\mathrm{d}V}{\mathrm{d}r} = \frac{\mathrm{d}}{\mathrm{d}r}\left(\frac{4}{3}\pi r^3\right) = 4\pi r^2$$

and after rearranging

$$\mathrm{d}V = 4\pi r^2 \mathrm{d}r.$$

Analogously, ist results for the surface:

$$\frac{\mathrm{d}A}{\mathrm{d}r} = \frac{\mathrm{d}}{\mathrm{d}r}\left(4\pi r^2\right) = 8\pi r$$

so that

$$dA = 8\pi r dr.$$

In equilibrium, the following is valid:

$$p_\sigma \cdot 4\pi r^2 dr = \sigma \cdot 16\pi r dr.$$

The resulting capillary pressure p_σ in a soap bubble is then

$$p_\sigma = \frac{4\sigma}{r} \tag{15.5}$$

which is, as expected, inversely proportional to the radius of the bubble.

Instead of a soap bubble, let us now consider a gas "bubble" (or more precisely a gas-filled cavity) in a liquid such as the "bubbles" in champagne or, possibly, a drop of a liquid. Now there is only one interface to be taken into account. Correspondingly, the capillary pressure is

$$p_\sigma = \frac{2\sigma}{r}. \tag{15.6}$$

Capillary pressure disappears for plane surfaces ($r \to \infty$), but for very small drops, it is quite important. For example, a drop of water with a radius of 1 μm has the capillary pressure of 146 kPa.

Vapor Pressure of Small Drops A bulk liquid is subject to a saturation vapor pressure of $p_{\mathrm{lg},r=\infty}$. As a result of capillary pressure, the chemical potential of a drop of liquid is higher by

$$\Delta\mu_1 = p_\sigma \cdot \beta = \frac{2\sigma}{r} V_\mathrm{m}$$

than that of a bulk liquid. This means that a decrease in the size of the drop increases its tendency to evaporate. Equilibrium with the vapor occurs when its chemical potential has also grown by the same difference $\Delta\mu_\mathrm{g}$ due to a raise of pressure from $p_{\mathrm{lg},r=\infty}$ to $p_{\mathrm{lg},r}$:

$$\Delta\mu_\mathrm{g} = RT \ln \frac{p_{\mathrm{lg},r}}{p_{\mathrm{lg},r=\infty}} = \frac{2\sigma}{r} V_\mathrm{m} = \Delta\mu_1.$$

We obtain

$$\ln\frac{p_{\mathrm{lg},r}}{p_{\mathrm{lg},r=\infty}} = \frac{2\sigma V_{\mathrm{m}}}{rRT}$$

and, respectively,

$$p_{\mathrm{lg},r} = p_{\mathrm{lg},r=\infty}\exp(2\sigma V_{\mathrm{m}}/rRT) \quad \text{Kelvin equation.} \tag{15.7}$$

Small drops have a higher vapor pressure $p_{\mathrm{lg},r}$ than that of a bulk liquid ($p_{\mathrm{lg},r=\infty}$). Table 15.3 illustrates the rise of vapor pressure as a function of the size of drops in the case of water drops.

Very small droplets are therefore quite unstable and the question arises of how condensation of water vapor in air can occur at all. There have to be "condensation nuclei," i.e., molecules, ions, dust particles, etc., with which even just a few water molecules can form stable aggregates that can continue to grow. If such nuclei or surfaces that water can precipitate onto are absent, supersaturated water vapor can exist for a very long time. Air for example can contain supersaturated water vapor even in a clear sky. This water vapor condenses on the particles left by the engine exhaust of an airplane and so-called condensation trails (contrails) appear behind the plane.

Capillary Action When a capillary tube is submerged in a wetting liquid, this liquid will rise in it up to a certain height. Experiment 15.4 is a good example for illustrating the dependency of capillary rise upon the diameter of the capillary tube.

Wetting of the inner wall of the capillary tube by the liquid film increases the liquid's surface. This is opposed by surface tension. A reduction of the surface can only occur if the liquid rises to a height h in the tube having a radius of r_{c} (Fig. 15.5). It forms a *meniscus* (the term for a curved surface in a narrow pipe). The meniscus of a completely wetting liquid, for example, water in a glass tube, assumes a hemispherical shape curved upward (concave surface). The water tries to cover as much of the glass surface as possible and the hemisphere is the smallest possible surface for the liquid. In the present case of a contact angle of $\theta \approx 0°$, the radius of curvature is equal to the capillary radius r_{c}. The liquid rises in the capillary until the weight $F_{\mathrm{G}} = mg = \rho Vg$ of the liquid drawn up the tube just compensates for the force F_σ resulting from surface tension along the capillary circumference. We obtain

Table 15.3 Increase of vapor pressure for varying sizes of water drops.

Radius (nm)	Number of particles	$p_{\mathrm{lg},r}/p_{\mathrm{lg},r=\infty}$
10^3	1.4×10^{11}	1.001
10^2	1.4×10^{8}	1.011
10	140,000	1.111
1	140	2.88

Experiment 15.4 *Capillary tubes in action*: A communicating system of several capillary tubes with varying diameters is filled with colored water. The water rises in the tubes due to the capillary effect and reaches different levels. The narrower the tube, the higher the water rises.

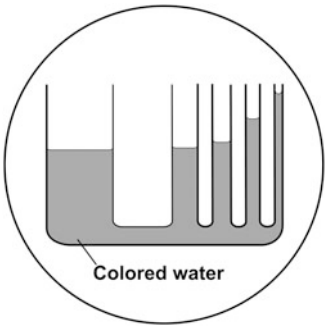
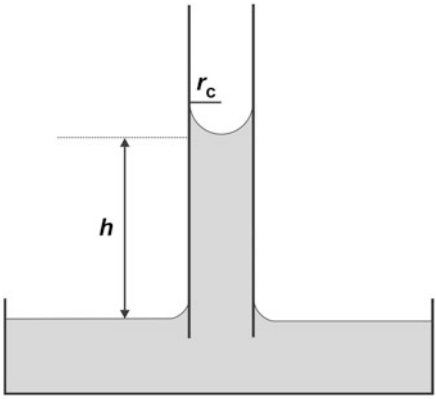


Fig. 15.5 A wetting liquid rising in a capillary tube (capillary rise).



$$F_\sigma = 2\pi r_c \sigma = \rho \pi r_c^2 h g = F_G$$

or after rearranging the terms

$$h = \frac{2\sigma}{\rho r_c g}, \tag{15.8}$$

where ρ stands for the density of the liquid. The capillary rise of a liquid is inversely proportional to the capillary radius. For a water-filled glass tube in air at standard conditions ($\sigma = 0.072$ N m^{-1} at 298 K, $\rho = 1{,}000$ kg m^{-3}, and $g = 9.81$ m s^{-2}), the height of the water column is

$$h = \frac{1.47 \times 10^{-5}}{r_c} \text{m}.$$

Thus for a tube with a radius of 2 cm, the water would rise only 0.7 mm, but for one with a radius of 0.2 mm, it would already rise to a height of 70 mm.

Moreover, the capillary rise of a liquid is directly proportional to the surface tension. This relation can therefore be used to determine the surface tension of liquids.

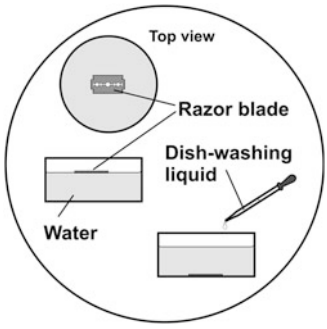
The capillary force works in the opposite direction for non-wetting liquids: The level of the liquid is lowered and it displays a convex surface. In this case, one speaks of a "capillary depression" (Example: mercury in a glass tube as in thermometers and barometers).

15.3 Adsorption on Liquid Surfaces

Dissolved substances can influence interface tension by enriching themselves in the interface. This phenomenon is called *adsorption*. The forces of attraction A–B between the molecules of the dissolved substance B and those of the solvent A are smaller than A–A, so that the dissolved substance is forced out of the interior of the phase. The characteristics of the interface are modified due to enrichment of the dissolved substance. The surface energy and therefore the surface tension decrease so that the capillary action increases. These types of substances are called *capillary active, surface active,* or *interface active*. They are also called *surfactants*. In aqueous solutions, this characteristic is exhibited mainly by organic compounds with long hydrophobic hydrocarbon chains and hydrophilic head groups [hydroxyl group, carboxylate group (COO^-), or sulfonic acid group $\left(SO_3^-\right)$].

An experiment using a razor blade shows the influence upon surface tension by surfactants of the kind found in dish-washing liquid (Experiment 15.5).

The surfactant molecules in the solution of a dish-washing liquid or a laundry detergent slip between the water molecules and the hydrophobic residue of these



Experiment 15.5 *Floating razor blade*: When a razor blade is carefully laid upon a water surface, it will sink slightly (comparable to a weight on a tensed membrane), but continues to float. When a solution of dish-washing liquid is added, the razor blade sinks to the bottom of the container because it can no longer be supported by the surface tension.

molecules then extend out of the water (Fig. 15.6). As a result, the attraction between the water molecules due to the strong hydrogen bridge bonds decreases along with surface tension.

If the concentration of the surfactant molecules continues to increase, the surface will finally become completely covered by a layer of molecules (monomolecular layer). If this concentration is exceeded, surfactant molecules will also be present in the interior of the liquid. However, they will be oriented so that the hydrophobic ends of the molecules are joined and shielded from the solution by the hydrophilic head groups. As a result, *micelles* are formed above a certain surfactant concentration, the so-called *critical micelle concentration* (CMC). Micelles are colloid-sized clusters.

The "*cleaning power*" of surfactants depends upon the hydrophobic hydrocarbon residues penetrating the dirt particles (drops of oil or grease, for example) and the textile fibers while the hydrophilic groups protrude into the water. The motion of the piece being washed separates the dirt particles from the fibers and solubilizes them. This means that their solubility in the solvent (in this case, water) is noticeably improved by adding a third chemical. Moreover, micelle formation is essential for the resorption of fat-soluble vitamins and the digestion of complicated lipids within the human body.

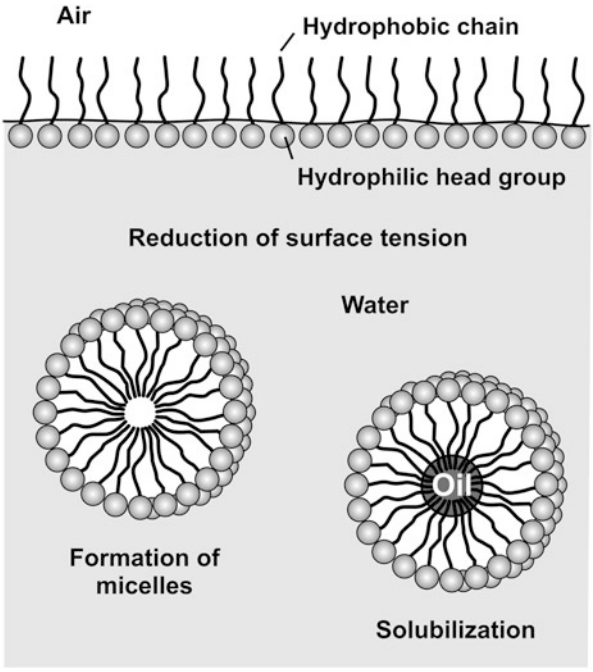


Fig. 15.6 Arrangement of surfactant molecules in a monolayer on the surface of water, formation of micelles, and emulsifying power of the surfactants.

15.4 Adsorption on Solid Surfaces

Physisorption and Chemisorption The phenomena of adsorption on solid surfaces are much more varied than those on liquid surfaces. A good example for observing these phenomena is activated carbon, a highly porous carbon with a large specific surface (300 to 2,000 $m^2\ g^{-1}$ carbon) and possessing excellent adsorption capacity (Experiment 15.6).

The actual process of adsorption happens to lie between two extreme forms of adsorption: *physical adsorption* (*physisorption*) and *chemical adsorption* (*chemisorption*). These differ from each other primarily by the strength of the bonding of the *adsorptive* (free particles before adsorption, gas molecules for example) to the *adsorbent*, i.e., the molecules of the solid surface (for clarity, compare to Fig. 15.7). The particles that have accumulated on the solid surface are called *adsorbate*.

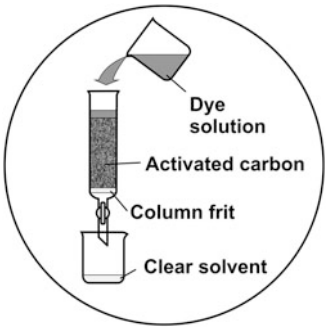
The term physisorption is used when the molecules of a gaseous or dissolved substance B that have accumulated on a solid adsorbent are loosely "physically" bound (Fig. 15.8, left) as might happen by Van Der Waals' forces:

$$\square + B_2 \rightarrow \boxed{B_2}.$$

The symbol $\square$ labels a site on the surface.

Physical adsorption with a chemical drive $\mathcal{A}$ of the order of 8 to 10 kG has the character of a *condensation*. The drive is determined almost exclusively by the type of substance being adsorbed. The adsorbed particles can attach into several layers, one on top of the other (multilayer adsorption), and essentially keep their structure. Noble gases, for example, would be physisorbed at low temperatures.

In the case of chemisorption, though, a stable "chemical" bond is formed. Chemical adsorption has the character of a *chemical reaction*, where the values for the drive can typically lie between 40 and 800 kG. The drive depends significantly upon the adsorbing solid substance involved. The molecular bond in the adsorbate having, at most, a single accumulated layer on the adsorbent (monolayer adsorption) can often be strongly altered so that the particles are in a very reactive state and can even dissociate (compare Fig. 15.8, right). The adsorptive bonding of



Experiment 15.6 *Adsorption on activated carbon*: When a dye solution is poured into one end of a column filled with activated carbon, the solvent will come out clear at the other end. This experiment can also be done with soft drinks containing food coloring, or even red wine.

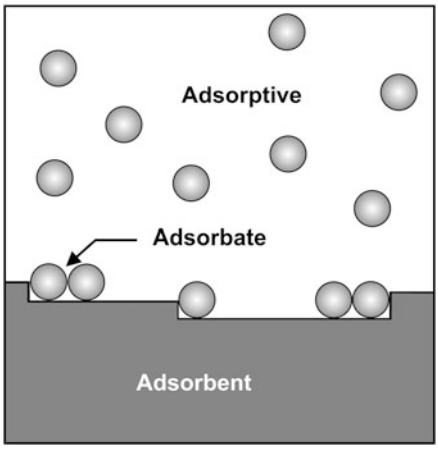


Fig. 15.7 Illustration of important terms describing adsorption.

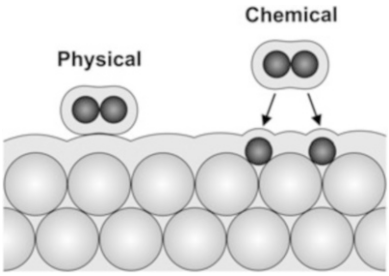


Fig. 15.8 Difference between physisorption and chemisorption.

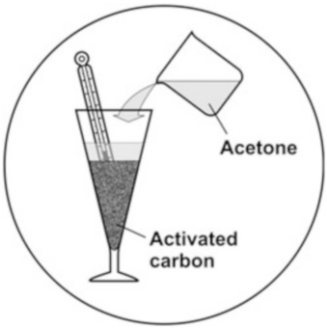
hydrogen to surfaces of transition metals such as Pd or Fe—which is important for catalytic reactions—is a typical case of chemisorption (see also Sect. 19.4). In this case, hydrogen is not adsorbed in molecular form but in its atomic form:

$$2\,\square + \mathrm{B}_2 \rightleftarrows 2\,\boxed{\mathrm{B}}.$$

$\square$ indicates a site on the surface able for chemisorption.

Adsorption is accompanied by a "heat effect" (Experiment 15.7). As always in chemical reactions, there are actually two effects at work. Energy is released and dissipated whereby entropy is generated: $S_\mathrm{g} = \mathcal{A} \cdot \Delta\xi/T$. This exothermal contribution is complemented by the (usually) exothermal latent entropy $S_\ell = \Delta_\square S \cdot \Delta\xi$ (the symbol $\square$ replaces the index R which we have commonly used to indicate chemical reactions). The reason for the latter is the fact that adsorption on a solid surface limits the mobility of the particles, resulting in the release of entropy.

Adsorption Isotherm We consider the adsorption of a substance B out of a gas or a solution on adsorption sites $\square$:



Experiment 15.7 *Rise of temperature in adsorption*: When acetone is poured over activated carbon, a noticeable rise in temperature occurs.

$$\square + \mathrm{B} \rightleftarrows \boxed{\mathrm{B}}.$$

If the temperature remains constant, an *adsorption equilibrium* will be established where the addition of particles B to and their elimination from the sites of adsorption both occur at the same rate. This is symbolized by a double arrow.

In the case of a gaseous adsorptive, the adsorbed amount n_B is dependent upon pressure p, and in the case of a dissolved adsorptive, it is dependent upon concentration c. The relation

$$n_B = f(p) \text{ or } n_B = f(c) \qquad T = \text{const.}$$

is called the equation of the *adsorption isotherm.*

In the case of the formation of a *monomolecular adsorption layer,* the *fractional coverage* Θ is often used instead of the *adsorbed amount* n_B to symbolize the extent of adsorption. It indicates the portion of the surface that is coated:

$$\Theta = \frac{n_B}{n_{B,\text{mono}}} = \frac{m_B}{m_{B,\text{mono}}}. \tag{15.9}$$

The simplest theoretical description of an isotherm is the so-called *Langmuir isotherm* which is based upon a model of equivalent and independent adsorption sites upon a homogeneous surface whereby adsorption cannot proceed beyond monolayer coverage. Although we have mostly been dealing with static aspects of chemical dynamics so far, we will derive this adsorption isotherm first by using kinetic aspects (in anticipation of Chap. 16).

Adsorption equilibrium is established when the rate r_{ads} of adsorption equals the rate r_{des} of *desorption*, meaning the release of already adsorbed molecules.

According to the concepts of kinetics, the rate of adsorption is proportional to the product of the concentrations of the reaction partners. In this case, these are the adsorptive and the free sites on the surface. Partial pressure p or molar concentration c can be used as the measure of adsorptive concentration. The concentration of free sites, on the other hand, must be proportional to the fraction of surface that is not covered, $1 - \Theta$. In summary, we have

$$r_{\text{ads}} = k_{\text{ads}} \cdot p \cdot (1 - \Theta), \tag{15.10}$$

whereby the proportionality constant k_{ads} can also be called the rate coefficient of adsorption. (We will deal with rate coefficients in Chap. 16 and again in more detail in Chap. 18.)

The rate of desorption is proportional to the concentration of sites that are already occupied and, therefore, the fractional coverage Θ. We obtain

$$r_{\text{des}} = k_{\text{des}} \cdot \Theta \tag{15.11}$$

with k_{des} as the rate coefficient of desorption.

The following is valid for dynamical equilibrium:

$$k_{\text{ads}} \cdot p \cdot (1 - \Theta) = k_{\text{des}} \cdot \Theta.$$

Solving for Θ yields:

$$\Theta = \frac{k_{\text{ads}} \cdot p}{k_{\text{des}} + k_{\text{ads}} \cdot p}. \tag{15.12}$$

Using $\overset{\circ}{K} = k_{\text{ads}}/k_{\text{des}}$ we obtain Langmuir's adsorption isotherm:

$$\Theta = \frac{\overset{\circ}{K} \cdot p}{1 + \overset{\circ}{K} \cdot p} \quad \text{for } T = \text{const.} \tag{15.13}$$

$\overset{\circ}{K}$ can be interpreted as the equilibrium constant for the process of adsorption. Correspondingly, $\overset{\circ}{K}$ is dependent upon temperature (compare Chap. 6).

At low pressures, $\overset{\circ}{K} \cdot p \ll 1$ applies; the isotherm then rises proportionally to p. At high pressures $\left(\overset{\circ}{K} \cdot p \gg 1\right)$, the fractional coverage asymptotically approaches the limiting value of 1 (Fig. 15.9).

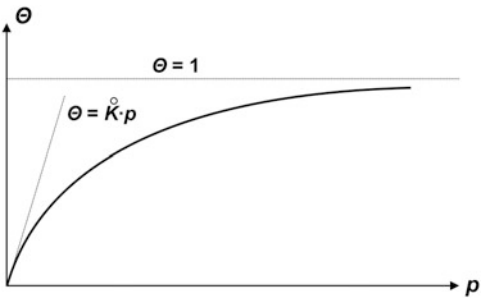


Fig. 15.9 Langmuir's adsorption isotherm.

We can also derive Langmuir's isotherm with the help of the chemical potential. In order to do this, we consider the following sequence of simple processes:

$Bs + H^+ \rightarrow BsH^+$,	Protonation of a base during a titration,
$E + B \rightarrow EB$,	Formation of an enzyme – substrate complex in a cell,
$\square + B \rightarrow \boxed{B}$,	Adsorption of a molecule at a surface site.

In Sect. 7.4, we dealt extensively with the first process and its description with the help of proton potential. A characteristic common to all three processes is that in each one, a certain type of particle occupies a certain type of site. There is obviously a smooth transition from the first type of process to the last one in the sequence because it is easy to insert additional intermediate links. For instance, the gap between the first *homogeneous* reaction and the third *heterogeneous* reaction can be bridged by the second which can be considered a bimolecular reaction between the dissolved substances E (enzyme) and B (substrate) as well as an adsorption of B at a site E. If we imagine the E-molecules to be combined into larger and larger two-dimensional complexes, we arrive in stages at a contiguous surface.

We therefore want to deal with the question of the chemical potential of *sites*. In order to do this, we will again consider adsorption of a substance B out of a gas or a solution on *independent* adsorption sites, but now from this new point of view:

$$\square + B \rightleftarrows \boxed{B}.$$

Adsorption equilibrium is determined by the free and occupied sites $\square$ and $\boxed{B}$, so it seems obvious to assign to them chemical potentials $\mu(\square)$ and $\mu\left(\boxed{B}\right)$. A comparison to the corresponding homogeneous reaction suggests an interesting idea:

$$A + B \rightleftarrows AB.$$

A particle A can be considered a *carrier* of a single adsorption site $\square$ for B. In order to keep the sites from influencing each other, the total concentration $c = c(A) + c(AB)$ of free and bonded A must remain low. This then allows us to apply the mass action equations for $\mu(A)$ and $\mu(AB)$ (compare Sect. 6.2). The condition for equilibrium $\mu(A) + \mu(B) = \mu(AB)$ therefore assumes the form

$$\overset{\circ}{\mu}(A) + RT\ln[c(A)/c^{\ominus}] + \mu(B) = \overset{\circ}{\mu}(AB) + RT\ln[c(AB)/c^{\ominus}]. \qquad (15.14)$$

In order to attain a description that is independent of whether a site sits upon separate particles or upon a continuous surface and is also independent of the parts of the carrier A that are inessential for adsorption, we slightly alter the condition for equilibrium. $c(A)/c \equiv \Theta(\square)$ is the *fraction of empty sites*, $c(AB)/c \equiv \Theta\left(\boxed{B}\right)$ is

the *fraction of occupied sites*. We replace c(A) and c(AB) by $c \cdot \Theta(\square)$ and $c \cdot \Theta\left(\boxed{\text{B}}\right)$ and subtract $\overset{\circ}{\mu}(\text{A}) + RT\ln(c/c^{\ominus})$ from both sides:

$$\begin{array}{c} \underbrace{\overset{\circ}{\mu}(\square) + RT\ln\Theta(\square)}_{\mu(\square)} + \mu(\text{B}) = \underbrace{\overset{\circ}{\mu}\left(\boxed{\text{B}}\right) + RT\ln\Theta\left(\boxed{\text{B}}\right)}_{\mu\left(\boxed{\text{B}}\right)} \\ \mu(\square) + \mu(\text{B}) = \mu\left(\boxed{\text{B}}\right) \qquad \text{(condition for equilibrium).} \end{array} \tag{15.15}$$

We consider $\overset{\circ}{\mu}\left(\boxed{\text{B}}\right) \equiv \overset{\circ}{\mu}(\text{AB}) - \overset{\circ}{\mu}(\text{A})$ to be *the basic value of the chemical potential of occupied sites* $\boxed{\text{B}}$, i.e., the potential $\mu\left(\boxed{\text{B}}\right)$ at full occupancy, $\Theta\left(\boxed{\text{B}}\right) = 1$. The term $\overset{\circ}{\mu}(\square) \equiv 0$ is only inserted for the sake of uniformity. It functions as the *basic value of the chemical potential of empty sites* $\square$, meaning the potential $\mu(\square)$ for $\Theta(\square) = 1$.

As a result of the bond between A and B, both A and B are altered. In the case of larger molecules, the changes primarily affect the atoms near the place of bonding; atoms that are farther away are hardly touched. The definition above of the quantity $\overset{\circ}{\mu}\left(\boxed{\text{B}}\right)$ boils down to the fact that all changes to molecules A and B are formally assigned to the *adsorbed* particles B. The contribution of the unaltered parts of the carrier A is canceled, especially the contribution by all atoms of A that are outside the sphere of influence of the bonding site.

We can now use the mass action equations shown above for *independent* sites,

$$\mu(\square) = \overset{\circ}{\mu}(\square) + RT\ln\Theta(\square) \tag{15.16}$$

and

$$\mu\left(\boxed{\text{B}}\right) = \overset{\circ}{\mu}\left(\boxed{\text{B}}\right) + RT\ln\Theta\left(\boxed{\text{B}}\right), \tag{15.17}$$

to describe the adsorption of a substance B out of a dilute solution or a dilute gas on a solid surface having equivalent adsorption sites—independently of whether or not they are occupied. Taking the mass action equation for B, $\square$ and $\boxed{\text{B}}$ into account, as well as the equations $\Theta\left(\boxed{\text{B}}\right) = \Theta$ and $\Theta(\square) = 1 - \Theta$ with *fractional coverage* Θ, the condition for adsorption equilibrium is:

$$\overset{\circ}{\mu}(\square) + RT\ln(1-\Theta) + \overset{\circ}{\mu}(\text{B}) + RT\ln(c/c^{\ominus}) = \overset{\circ}{\mu}\left(\boxed{\text{B}}\right) + RT\ln\Theta. \tag{15.18}$$

We subtract $\overset{\circ}{\mu}\left(\boxed{\text{B}}\right)$ from both sides, move the logarithmic terms to one side, divide by RT, take the exponential, and divide by $c^{\ominus}$. Because of $\overset{\circ}{\mu}(\square) = 0$, this leads to the relation

$$\underbrace{\frac{1}{c^{\ominus}} \cdot \exp\left(\frac{\overset{\circ}{\mu}(\mathrm{B}) - \overset{\circ}{\mu}\left(\boxed{\mathrm{B}}\right)}{RT}\right)}_{\overset{\circ}{K}} = \frac{\Theta}{(1-\Theta)\cdot c}. \tag{15.19}$$

Here, $\overset{\circ}{K}$ is the equilibrium constant, for which (according to Sect. 6.4) the following is valid:

$$\overset{\circ}{K} = (c^{\ominus})^{\nu}\,\overset{\circ}{\mathcal{K}} = (c^{\ominus})^{-1}\exp\left(\frac{\overset{\circ}{\mu}(\mathrm{B}) - \overset{\circ}{\mu}\left(\boxed{\mathrm{B}}\right)}{RT}\right) \quad \text{with} \quad \nu = -1.$$

Transformation of Eq. (15.19) finally results in the familiar equation for Langmuir's adsorption isotherm

$$\Theta = \frac{\overset{\circ}{K}\cdot c}{1 + \overset{\circ}{K}\cdot c}. \tag{15.20}$$

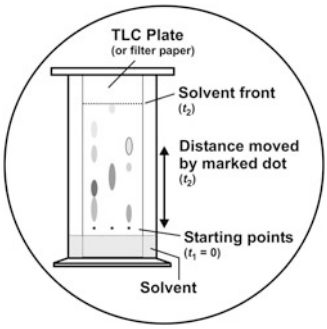
15.5 Applying Adsorption

Surface Measurement The specific surface of a porous solid material can be determined from the adsorbed amount of an adsorptive when its surface demand is known. The most reliable method for doing this is based upon the physisorption of gases (mostly nitrogen) near their boiling points. The so-called BET isotherm is used for the analysis. This isotherm developed in 1938 by Brunauer, Emmet, and Teller takes multilayer adsorption into account as well.

Separation of Substances Adsorption also plays a major role in separation of substances, especially in *adsorption chromatography*. The method is based upon the difference of adhesion probabilities of the substances being separated which, being in a mobile phase (liquid, gas), are passed along a stationary phase (solid material, for example, Al_2O_3, SiO_2). The greater the attraction of a substance for the stationary phase compared to the mobile phase, the slower this substance moves up. We differentiate between *gas–solid chromatography* (GSC) and *liquid–solid chromatography* (LSC). Depending upon the method in use, we also distinguish between column chromatography, paper chromatography, or thin-layer chromatography. A simple yet convincing example from everyday life is the chromatographic separation of felt pen ink (Experiment 15.8).

The same dye in the same solvent will always move the same distance in the same period of time. The individual components can therefore be characterized by the R_f value (R_f stands for "retention factor"):

Experiment 15.8 *Chromatographic separation of black felt pen ink*: Different black felt tip pens are used to make dots along a line near the bottom edge of a thin-layer chromatography (TLC) plate covered with silica gel for thin-layer chromatography. The bottom edge of this plate is then put into a TLC chamber (or a beaker) containing a few centimeters of water as solvent. A separation of the black ink into variously colored components (for example, violet, yellow, blue) can soon be observed. Instead of a TLC plate, a strip of filter or blotting paper can also be used.



$$R_f = \frac{\text{Distance starting line} - \text{center of dot}}{\text{Distance starting line} - \text{solvent front}}.$$

Heterogeneous Catalysis Adsorption is the basis of heterogeneous catalysis, which makes it especially important to industrial production processes. This will be gone into more detail in Sect. 19.4.